Surface active agents (surfactants) are amphiphilic compounds containing one hydrophobic part that has affinity for nonpolar media and other the hydrophilic part having affinity for aqueous media. The hydrophobic portion of a surfactant is generally a long hydrocarbon chain often referred to as ‘nonpolar tail’ while the hydrophilic group is polar and is referred to as the ‘polar head’. Surfactants are used in many industries such as soaps, detergents, cosmetics, foods, paints, pharmaceuticals, petroleum, textiles, etc. as emulsifiers/demulsifiers, foaming/defoaming agents, wetting, solubilizing and dispersing agents. These substances reduce the surface tension of water by adsorbing at the air-water interface and self-assemble to form micelles. Spherical micelles form at concentration, above the critical micelle concentration (CMC) which may grow to ellipsoidal, cylindrical or thread-like micelle, disk-like micelle and vesicles under different solution conditions.

The size and shape of micelles primarily depends on hydrocarbon tail, polar head group, counter ion and spacer (in case of gemini surfactants) in aqueous media [1, 2]. The aggregation behaviour of micelles can also be modified by the small changes in the solution conditions such as surfactant concentration, ionic strength, additives, pH and temperature. The effect of electrolytes on ionic micelles has been widely studied [3- 5]. Addition of hydrotropes to micellar solutions may initiate micellar growth and transform the micellar microstructure into different morphologies [6-8]. Changes in micelle size, shape and aggregation depend on the solubilization of additives in micelle. In solubilization, the location and interaction of solubilizate within micelle play significant role to induce micellar change. Solubilization of weakly polar compounds like phenols [9-11], aromatic amines [12], aromatic acids [13-15] and alcohols [16] in cationic surfactant solution and their effect on micellar transition have been examined. Weakly polar aliphatic compounds like medium chain alcohols [17-19], amines [20, 21] and carboxylic acids [22, 23] have shown a remarkable effect on micellar growth and transition.

Hence, the aim of this work is to investigate the micellar and solubilization behaviour of surfactants in presence of different kind of weakly polar additives like alcohols, glycol ethers phenols, aromatic bases, acids etc. by using techniques like physico-chemical methods (cloud point, viscometry) and instrumental methods like spectral [UV-Visible, nucler magnetic

resonance (NMR)] and scattering [dynamic light scattering (DLS) and small angle neutron scattering (SANS)].

In my research work, I report the growth in cationic micelles induced by the presence of p-toluidine (PTD) using a number of different techniques. Representative cationic surfactants were chosen for their tendency to form worm-like micelle under favorable conditions (e.g cetyltrimethylammonium bromide or CTAB) versus those that are unlikely to form worm-like aggregates (e.g. dodecyltrimethylammonium bromide or DTAB). The solubilities of PTD in various cationic surfactant micelles and viscosity as well as dynamic light scattering results for cationic surfactants with different counterion, chain length and head group have been reported. The location of PTD in micelle and the interactions with surfactant were examined by ^{1}H NMR experiments and 2D NOESY (nuclear Overhauser effect spectroscopy).

In other study, aqueous micellar solutions of cationic gemini surfactants (dimeric surfactants) belonging to 12-s-12 series (where s = 4, 5, 6) have been examined in the presence of PTD which exhibit a noticeable micellar growth/transition from viscometric and scattering studies. Micellar growth induced by the incorporation of the p-toluidine (PTD) in micelles of 12-s-12 depends not only on the solution conditions and the functional group present in the additive but also gets influenced by the spacer chain length of surfactant. This study offers a large body of important information on micellar growth and possible shape transition as inferred from capillary viscometry and scattering techniques. The DLS and SANS studies showed pronounced micelle growth around pH 5-6 in the presence of PTD. The possible reason is attributed in terms of adsorption, surface charge density, chemical environment and orientation of PTD molecules in the micelle. 2D NOESY spectra provide clear idea on the site of PTD encapsulated in 12-4-12 micelles.

Changes in pH of aqueous micellar solutions alter the micellar behavior of pH responsive surfactants such as zwitterionic [24, 25], alkyldimethylamine oxide [26, 27] and particularly polymeric surfactants [28, 29] and show interesting solution behavior. Some pH responsive polymeric surfactants have been studied for controlled release of drugs [30, 31]. For non-pH responsive surfactants, their aggregate morphology can be tuned by adding some pH responsive compounds in their solution. There are few reports on the micellar behavior of pH insensitive conventional surfactant such as CTAB [32, 33 34] and Triton-X 100 [35] in the presence of pH responsive polar aromatic compounds.

In the present study, pH controlled solubilization of PTD in micelles of surfactants having dissimilar head group charge is examined. A connection is revealed between viscosity enhancement and locus of solubilized PTD on the micelles of different surfactants viz. dodecyl trimethylammonium bromide (DTAB, cationic), sodium dodecyl sulfate (SDS, anionic) and dodecyl-N,N-dimethyl-3-amino-1-propane sulfonate (DDMPS, zwitterionic), dodecyl-dimethyl amine oxide (DMDAO, cationic-nonionic) and p-tertoctylphenoxy polyethylene (9.5) ether, Triton X-100 (nonionic) micelles were examined by viscosity, dynamic light scattering and 2D NOESY. PTD works as cationic hydrotrope in acidic pH and remains neutral in basic pH. DTAB and DDMPS did not show any significant growth with solubilized p-toluidine, while pH dependant micellar growth/transitions were observed for SDS, DMDAO and Triton X-100. Dissimilar effects were observed for different surfactants; DMDAO micelles showed maximum growth at pH ~5.0-6.0 with almost no effect in more acidic pH, SDS micelles grew only in acidic conditions, while Triton X-100 micelles grew more in basic media. The effect of temperature on DMDAO and Triton X-100 micelles in the presence of PTD was also examined. The location of PTD in micelle was obtained from 2D-NOESY.

One of the important phenomena of the surfactant is phase/clouding behaviour. Clouding phenomenon generally occurs with polyoxyethylated nonionic surfactants. Clouding behaviour is a typical physical change in solutions of these amphiphilic substances where the solution separates into a surfactant-rich and a surfactant-poor phase at a definite temperature. Polyoxyethylene type nonionic surfactants are widely used in household- [36, 37], chemical-[36, 38] and pharmaceutical industries [39, 40]. Therefore the cloud point data are of considerable practical interest. The cloud point and micelle size/shape of nonionic surfactant in aqeous solution is influenced by the presence of electrolytes and nonelectrolytes [41, 42]. Hence, the aim is to investigate the micellar and solubilization behaviour of nonionic surfactants in presence of different kind of weakly polar additives like alcohols, glycol ethers, phenols and bisphenol A.

Here, micellar characteristics of nonionic surfactant p-tert-octyl-phenoxy polyethylene (9.5) ether (Triton X- 100) in aqueous media containing mono ethyl-, mono n-butyl- and mono n-hexyl ethers of ethylene glycol and diethylene glycol (and the corresponding alcohols viz. ethyl, n-butyl, n-hexyl alcohol) were examined. The micelle size increased with the addition of C_6E_m and decreased when C_2E_m alcohols were added to Triton X-100 solution; the increase and decrease in the micellar size in the presence of varying amounts of C_4E_m alcohols depends on

the number of polar ethoxylate groups. The results are supported by viscosity and cloud point data and explained on the basis of solvophobic interaction. The interaction and location of additives in micelles is examined by ^{1}H NMR and 2D NOESY. The studies indicate that C_2E_m molecules mostly remain in bulk water; C_6E_m molecules get solubilized toward the core of the aggregates, while C_4E_m molecules are localized in the shell region of micelle according to their octanol/water partition coefficient values.

In another study micellar characteristics of Triton X- 100 in the presence of six phenols e.g. phenol, p-cresol, 1-naphthol, catechol, quinol and resorcinol have been examined. Cloud point, viscosity and dynamic light scattering data on aqueous micellar solutions of Triton X-100 in the presence of these phenolic solutes are reported. The effect of temperature and pH on size of TX-100 micelles with solubilized phenols was studied. Hydrophilic catechol, quinol and resorcinol did not show much change in size while more hydrophobic 1-naphthol, p-cresol and phenol induced remarkable micellar growth which further enhanced at higher temperature and low pH. The interaction and location of p-cresol and quinol in micelle were examined from ^{1}H NMR and 2D NOESY.

There has been considerable interest over the past few years in designing dimeric/oligomeric surfactants and as a result gemini surfactants emerged as potentially useful substances [2, 43]. Likewise polymeric surfactants have become important in recent years; Ethylene oxide-propylene oxide block copolymers with trade name pluronic® have been most extensively studied surfactants from this clan [36, 44]. However, oligomeric surfactants have not been studied in detail. Some dimers/oligomers show high viscosity at relatively low concentration in aqueous media due to self-assembly to large aggregates [45, 46]. As an oligomeric surfactant, Tyloxapol [4-isooctylpolyoxyethylenephenol-formaldehyde polymer] shows considerable distinction in the physico-chemical properties from monomeric surfactant Triton X-100 [41, 47].

In the present study, the influence of oligomeric structure of Tyloxapol on micellar characteristics is compared with corresponding standard monomeric surfactant Triton X-100. The focus has been to compare the solubilization of commercially important compound bisphenol-A (BPA, also an endocrine disruptor) in these two nonionic surfactants and its effect on micellar evolution. Micellar/clouding characteristics of Triton X-100 and Tyloxapol solutions were determined by DLS and SANS. These techniques were used to examine the solubilization

of BPA in micellar solutions with the support of additional methods like viscometry and UV-Visible spectroscopy. The results indicate that 5% Triton X-100 in water at 30°C forms ellipsoidal micelles while small spherical are formed in 5% Tyloxapol. More BPA was solubilized in Tyloxapol micelles; the molar solubilization ratio (MSR) and micelle-water partition coefficient (K_m) were higher than for Triton X-100 micelles. BPA induced micelle growth was seen for both the surfactants which caused noticeable change in phase behaviour, viscosity and shape/size of micelles. Small spherical Tyloxapol micelles transform into ellipsoidal ones while the ellipsoidal Triton X-100 micelles transform to short rods/stretched ellipsoidal structures. Micellar/phase behaviour for BPA solubilized micelles was markedly dependant on the pH of solution.

The research work of M.Phil. describes the application of nonionic surfactant for removal of dye by using colud point extraction method. This extraction is dependant on surfactant concentration, temperature and pH. The additives like salts and glycol ethers were used to improve extraction of dye by this method.

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